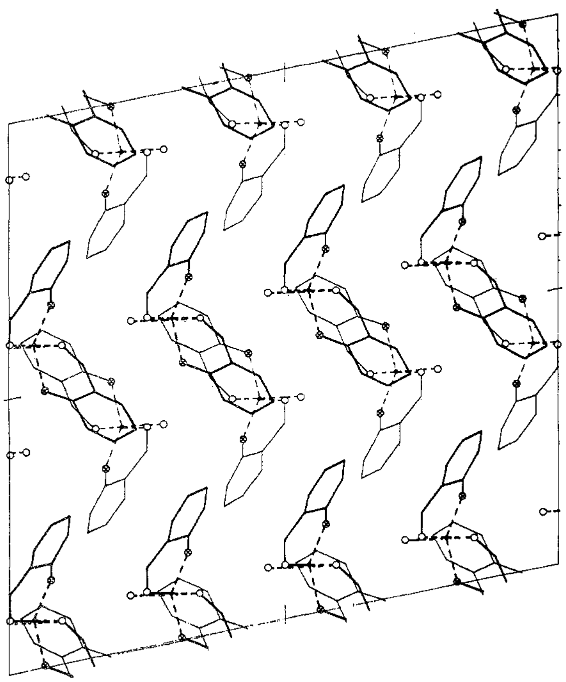

Figure 2.—Molecular packing in Ni(Saldipa).

a methyl group has replaced the proton on the secondary amine. While this is a small perturbation with respect to the entire molecule, it appears that the introduction of this methyl group has a significant effect on the geometry of the first coordination sphere, as evidenced by a somewhat more regular arrangement of the nitrogen and oxygen atoms around the nickel atom in Ni(SalMeDPT) than in Ni(Saldipa). For Ni(SalMeDPT) the angles in the equatorial plane are O–Ni–O′ = 142°, O′–Ni–N = 105°, and N–Ni–O = 113°,[11] while in Ni(Saldipa) the corresponding angles are $O_1$–Ni–$O_2$ = 145.7 (2)°, $O_2$–Ni–$N_1$ = 102.5 (2)°, and $N_1$–Ni–$O_1$ = 111.4 (2)°. Analogous bond distances in the two structures agree quite well.

The geometry of Ni(Saldipa) is in clear contrast to the structure of the Schiff's base complex $Ni[O(5\text{-}Cl\text{-}C_6H_3)CH{=}NC_2H_4N(C_2H_5)_2]_2$. This complex has been shown to have a distinctly square-pyramidal configuration.[12] Here two nitrogen and two oxygen atoms form a square plane and the Ni atom is somewhat out of the plane. An apical nitrogen then completes the coordination polyhedron.

**Acknowledgment.**—This work has been supported in part by NSF Grants GP 7920 and GP 15432.

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# The Crystal and Molecular Structure of the Mixed Sandwich Complex π-Cyclopentadienyl-π-triphenylcyclopropenylnickel, $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$

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The crystal and molecular structure of π-cyclopentadienyl-π-triphenylcyclopropenylnickel, $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$, has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes as discrete molecular units in the orthorhombic space group $Pna2_1$ with four molecules per unit cell of dimensions $a$ = 21.003 (1), $b$ = 12.3596 (7), and $c$ = 7.4959 (5) Å. The measured and calculated densities are 1.32 (1) and 1.328 g cm$^{-3}$, respectively. The structure has been refined by full-matrix least-squares methods to a conventional $R$ factor of 0.056 for the 1751 intensities above background. The nickel atom is complexed in a sandwich fashion between the parallel cyclopentadienyl and triphenylcyclopropenyl rings, the averages of the nickel–carbon distances being 2.100 (6) and 1.961 (4) Å, respectively, for the two rings. Average C–C distances were 1.405 (9) Å for the cyclopentadienyl ring and 1.428 (5) Å for the cyclopropenyl ring. The phenyl groups are bent and twisted out of the plane of the cyclopropenyl ring in "propeller" fashion. Disorder was found in the cyclopentadienyl ring.

## Introduction

An area of continuing interest in the field of organometallic chemistry is that of π-bonded "sandwich" complexes of the transition elements. The vast majority of complexes of this nature obey the well-known noble gas formalism. This rule suggests that an isoelectronic series of mixed sandwich compounds[1] containing a cyclopentadienyl ring and carbocyclic rings of varying sizes should exist—namely, $(\pi\text{-}C_5H_5)Cr(\pi\text{-}C_7H_7)$,[2] $(\pi\text{-}C_5H_5)Mn(\pi\text{-}C_6H_6)$,[3] $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_5)$,[4,5] $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_4R_4)$ where R = H[6,7] and $C_6H_5$,[8,9] and $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3R_3)$ where R = H[10] and $C_6H_5$.[11,12] With the exception of ferrocene, no crystallographic data

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(10) This complex is presently unknown, although the cyclopropenium cation has been synthesized: R. Breslow and J. T. Groves, *ibid.*, **92**, 984 (1970).

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have been reported in this series and the only X-ray study of a mixed sandwich compound to date has been of $(\pi\text{-}C_5H_5)V(\pi\text{-}C_7H_7)$.[13,13a] It is felt that structural data on mixed complexes of this type where the metal atom is in a less symmetrical environment might give further insight into the bonding of carbocyclic ring systems to transition metals. For this reason and in keeping with our continued interest[11,14,15] in the structure and bonding of transition metal complexes of the triphenylcyclopropenyl ligand, we have undertaken an X-ray crystal analysis of $\pi$-cyclopentadienyl-$\pi$-triphenylcyclopropenylnickel, $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$.[11]

## Collection and Reduction of X-Ray Data

A sample of $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$, kindly supplied by Professor M. D. Rausch, was recrystallized from an ethanol–hexane mixture to yield deep red-orange prisms suitable for X-ray studies. Precession and Weissenberg photography established that the crystals belonged to the orthorhombic system. The observed systematic absences $0kl$, $k + l$ odd, and $h0l$, $h$ odd, are consistent with either space group $Pna2_1$ ($C_{2v}^9$) or $Pnam$ (which is an alternate setting of $Pnma$ ($D_{2h}^{16}$)). Subsequent refinement results confirm the correctness of the former space group. Least-squares treatment of $2\theta$ values for 16 reflections ($64° < 2\theta < 108°$) carefully centered on a GE XRD-5 diffractometer using Cu K$\alpha_1$ radiation ($\lambda$ 1.5405 Å) and a takeoff angle of 2° gave the following values for the unit cell constants: $a = 21.003$ (1) Å, $b = 12.3596$ (7) Å, and $c = 7.4959$ (5) Å. The density of 1.32 (1) g cm$^{-3}$, measured by flotation in an aqueous solution of potassium iodide, agrees well with a calculated value of 1.328 g cm$^{-3}$ for four molecules in the unit cell.

Intensity measurements were made at 20° on a red-orange crystal mounted on a fiber with dimensions $0.18 \times 0.28 \times 0.33$ mm along $a$, $b$, and $c$. This crystal was placed on a GE XRD-5 diffractometer with [001] parallel to the $\varphi$ axis. The crystal had 12 distinct faces; all face planes of the type $\{100\}$, $\{110\}$, and $\{011\}$ as well as (101) and $(\bar{1}01)$ were identified and measured for absorption correction purposes. A kinematic intensity profile[16] was obtained by the $\omega$-scan technique for several typical reflections. For a takeoff angle of 4°, the maximum width at half-maximum intensity was 0.43°.

Diffraction intensities were collected by the $\theta$–$2\theta$ scan method with a symmetric scan range of 3° ($0° < 2\theta \leq 120°$) and 4° ($120 < 2\theta \leq 140°$) and a scan rate of 2° min$^{-1}$. Ten-second stationary-crystal, stationary-counter background counts were taken at the lower and upper limits of the scan range. In order to reduce fluorescence of the nickel atom in the crystal, the primary beam was filtered through a 0.35-mil thickness of Ni foil. This Cu K$\alpha$ radiation was used to collect intensity data with the pulse height analyzer set for approximately a 90% window when centered on the Cu K$\alpha$ peak. Crystal and electronic stability were monitored by three standards which exhibited a uniform 4.8% decrease during the data collection period and all reflections were linearly corrected for this decrease. Apparently, a very slight amount of crystal decomposition occurred. Thirty reflections which had intensities that exceeded the linear range of the counter were remeasured using a reduced current on the X-ray tube.

A complete set of 2153 independent reflections within the $hkl$ octant having $2\theta \leq 140°$ ($(\sin \theta)/\lambda \leq 0.61$) were collected. Thirty additional Friedel related reflections of the form $\overline{hkl}$ were measured in an effort to determine the chirality of the crystal for the polar space group $Pna2_1$. All intensities were reduced to values of $F^2$ by correction for background, Lorentz, polarization, and absorption[17] effects. Standard deviations for each reflection were obtained using the formula

$$\sigma(I) = [C + 0.25(t_C/t_B)^2(B_1 + B_2) + (PI)^2]^{1/2}$$

where $C$ is the total integrated count in time $t_C$, $t_B$ is the time required for each background count $B_1$ and $B_2$, $P$ is a factor that corrects for random fluctuations present during data collection, and $I$ is the net integrated intensity. $P$ was chosen to be 0.05. There were 1760 independent reflections for which $I > 2.0\sigma(I)$ and these were used in the solution and refinement of the structure. For Cu K$\alpha$ radiation the linear absorption coefficient is 16.3 cm$^{-1}$ and the absorption corrections showed that the transmission coefficients ranged from 0.695 to 0.788 for this crystal.

## Solution and Refinement

The nickel atom was located from a three-dimensional unsharpened Patterson function. Structure factors and a Fourier electron density map phased on the nickel atom showed the positions of the three carbon atoms of the cyclopropenyl ring. A cycle of least-squares refinement phased on these four atoms gave an $R_1$ of 34.9% and $R_2$ of 45.1%. All full-matrix least-squares refinements were on $F$ and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights, $w$, were equal to $4F_o^2/\sigma^2(F_o^2)$. The conventional agreement factors were defined by $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. Scattering factors used for nickel, carbon, and hydrogen were those of Cromer and Waber,[18] Ibers,[19] and Stewart, *et al.*,[20] respectively. The nickel atom scattering factor was corrected for the real ($\Delta f' = -3.20$) and imaginary ($\Delta f'' = 0.67$) components[21] of anomalous

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(13) G. Engebretson and R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 481 (1963).

(13a) NOTE ADDED IN PROOF—The X-ray structure of another mixed sandwich complex, $(\pi\text{-}C_5H_5)Ti(\pi\text{-}C_8H_8)$, has recently been determined: P. A. Kroon and R. B. Helmholdt, *J. Organometal. Chem.*, **25**, 451 (1970). These authors found approximately constant titanium–carbon atom distances for the two different carbocyclic rings [Ti–$C_5H_5$ = 2.353 (2) Å and Ti–$C_8H_8$ = 2.323 (3) Å] while the perpendicular Ti–ring distances vary [Ti–$C_5$(ring) = 2.04 Å and Ti–$C_8$(ring) = 1.45 Å]. The opposing trends (*vide infra*) of constant perpendicular metal–ring distances found in $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$ *vs.* the constant metal–carbon distances found in $(\pi\text{-}C_5H_5)V(\pi\text{-}C_7H_7)$ and $(\pi\text{-}C_5H_5)Ti(\pi\text{-}C_8H_8)$ may be rationalized by assuming that different types of metal–ring bonding predominate in the two cases. Presumably for small ($C_3$) rings bonded to a metal atom $a_1$ interactions, molecular orbitals directed at the ring center, predominate whereas for large ($C_7$ and $C_8$) rings e type interactions, molecular orbitals directed at the ring perimeter, are most important. $C_4$, $C_5$, and $C_6$ rings would then represent intermediate cases which fill out the spectrum from $a_1$ to e predominance.

(14) D. L. Weaver and R. M. Tuggle, *J. Amer. Chem. Soc.*, **91**, 6506 (1969).

(15) R. M. Tuggle and D. L. Weaver, *ibid.*, **92**, 5523 (1970).

(16) L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, **15**, 983 (1962).

(17) P. Coppens, L. Leiserowitz, and D. Rabinovich, *ibid.*, **18**, 1035 (1965).

(18) D. T. Cromer and J. T. Waber, *ibid.*, **18**, 104 (1965).

(19) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(20) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(21) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

dispersion for Cu K$\alpha$ radiation. All computations were made in space group $Pna2_1$ since the assumption of $Pnam$ symmetry would have required the nickel atom to lie on a mirror plane parallel to the aromatic rings. This latter possibility was considered highly unlikely from a chemical standpoint provided there is not a high degree of disorder present in the crystal. Successful refinement (*vide infra*) confirms $Pna2_1$ as the correct choice.

Additional structure factor calculations and difference Fourier maps revealed the locations of the remaining carbon atoms although evidence for disorder and/or high thermal motion was observed in the cyclopentadienyl (Cp) ring region. The nickel and three carbon atoms of the cyclopropenyl rings were assigned anisotropic temperature factors and three cycles of least-squares refinement on all parameters reduced $R_1$ and $R_2$ to 0.086 and 0.101, respectively. Fifteen peaks (0.29–0.53 e$^-$/Å$^3$) in reasonable locations for phenyl group hydrogen atoms were seen on a difference Fourier synthesis phased on these structure factors. The hydrogen atoms were included in three further cycles of least-square calculations in which all parameters were varied except the hydrogen atom thermal parameters; these were fixed at a value for $B$ of 1 Å$^2$ greater than the carbon atoms to which they were bonded. This stage of the refinement converged to give values of $R_1 = 0.077$ and $R_2 = 0.085$.

Careful examination of a difference Fourier phased on these structure factors showed five peaks consistent with either disorder or considerable librational motion of the Cp ring. Four of these peaks (0.65–0.45 e$^-$/Å$^3$) were the highest on this map. Five additional weaker "ghost" peaks (0.45–0.21 e$^-$/Å$^3$) were seen in the cyclopropenyl ring region which presumably resulted from reflection across a pseudo mirror plane that passed through the nickel atom. Furthermore, refinement results at this point gave a large range (1.45 (1)–1.54 (1) Å) for the three apparently equivalent carbon–carbon distances in the cyclopropenyl ring. A staggered disordered model was employed for the Cp ring by inclusion of the five peaks noted in this section of the difference Fourier map. Six more cycles of least-squares refinement were calculated in which all parameters were varied except the occupancy factors of the carbon atoms for the two staggered rings. However, following each cycle the occupancy factors were readjusted by hand subject to two constraints: (1) that the sum of the two ring occupancy factors must equal unity and (2) that the mean temperature factor of the atoms in each ring must be identical. Presumably a more elegant treatment of the Cp ring would involve a hindered-rotor model.[22] Nevertheless, a particularly satisfying result of our refinement is the considerable reduction in the spread (1.421 (8)–1.437 (8) Å) of the three cyclopropenyl carbon distances. In addition, the carbon–carbon distances within the Cp ring, with the exception of two, are quite reasonable. The final cycle of refinement converged to give values of $R_1 = 0.0628$ and $R_2 = 0.0748$ and a 60/40 disorder for the Cp ring.

For the space group $Pna2_1$, two polarities for the crystal structure are possible—the one just determined (A) and the reversed polarity structure (B). In order to test the possibility that polarity B was correct, signs of the $z$ coordinates for all atoms in model A were reversed and this structure was refined in exactly the same manner as before. The $-z$ refinement converged to give values of $R_1 = 0.0635$ and $R_2 = 0.0757$. Application of a significance test on the $R_2$ factor ratios[23] indicates that polarity A is preferred at more than a 99.5% confidence level assuming that there are no systematic errors in our data. A comparison of the bond distances obtained from the two refinements shows, as expected, essentially no differences (within 0.7$\sigma$) for carbon–carbon distances in the aromatic rings since all of these bonds are very nearly perpendicular to the $c$ direction. However, choice of the incorrect chirality for the crystal (model B) and allowance for anomalous dispersion of the nickel atom causes the two rings to be shifted, relative to the fixed nickel atom, by 0.031 Å along the $z$ direction. The imaginary component of the anomalous scattering of Cu K$\alpha$ radiation by nickel is minor and the change in $z$ coordinates is accordingly small and in reasonable accord with the value of 0.022 Å predicted by use of an approximate formula due to Cruickshank and McDonald.[24] A comparison[25] of the ratios $|F_o(hkl)|/|F_o(\bar{h}\bar{k}\bar{l})|$ with $|F_c(hkl)|/|F_c(\bar{h}\bar{k}\bar{l})|$ for the 30 Bijvoet reflection pairs collected shows no preference for the structure of A polarity, nor do the ten most "sensitive" reflections, selected by use of the function[26] $D = [|F_o(hkl)| - |F_o(\bar{h}\bar{k}\bar{l})|]^2/\sigma^2(F_o(hkl))$, show such a preference. This is perhaps not surprising in view of the small differences in atom positions for the two different polarity structures. It should be emphasized here that, unlike some previous structures,[27,28] the differences in bond lengths between the two refinements are minimal and of no chemical significance.

Nine low-order reflections had values of $|F_o| < |F_c|$ and were obviously suffering from secondary extinction. These reflections were removed and three final cycles of least-squares refinement converged to give values of $R_1 = 5.6\%$ and $R_2 = 7.1\%$. In the last cycle of refinement the maximum change in a nonhydrogen parameter was 0.24$\sigma$ and the average change was 0.02$\sigma$. The final goodness of fit, $[\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$, was 2.19 e$^-$. This rather high value is presumably due to an overestimation of the absolute weights and/or the simplified model used for the disordered Cp ring. The highest peak in a final difference Fourier map ($\sigma(\Delta\rho)$[29] $= 0.08$ e$^-$/Å$^3$) was 0.38 e$^-$/Å$^3$ and in the vicinity of the nickel atom. A last structure factor calculation with the unobserved reflections included gave two reflections for which $|F_c|$ was twice the minimum observable value. Major programs used in the solution of the structure were Prewitt's SFLS-5 for structure factor and least-squares refinement calculations and Zalkin's FORDAP for Patterson and Fourier synthesis.

The positional and thermal parameters obtained in

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[23] W. C. Hamilton, *ibid.*, **18**, 502 (1965).

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[29] H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons Ltd., London, 1953, p 308.

TABLE I

Final Positional and Thermal Parameters[a]

| Atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Ni | 0.16575 (4) | 0.22923 (7) | $^1/_4$[b] | 3.07[c] |
| C(10) | 0.1459 (3) | 0.1730 (5) | 0.4872 (8) | 2.76[c] |
| C(11) | 0.1091 (3) | 0.0808 (4) | 0.5545 (8) | 2.79 (9) |
| C(12) | 0.0516 (3) | 0.0961 (5) | 0.6401 (9) | 3.21 (10) |
| C(13) | 0.0186 (3) | 0.0091 (6) | 0.7082 (10) | 4.38 (4) |
| C(14) | 0.4586 (3) | 0.4049 (6) | 0.1091 (10) | 4.50 (13) |
| C(15) | 0.4012 (4) | 0.3897 (6) | 0.5990 (12) | 5.02 (15) |
| C(16) | 0.3684 (3) | 0.4773 (5) | 0.0326 (10) | 4.01 (12) |
| C(20) | 0.1502 (3) | 0.2883 (4) | 0.4889 (8) | 2.80[c] |
| C(21) | 0.1228 (2) | 0.3889 (4) | 0.5527 (8) | 2.86 (9) |
| C(22) | 0.1593 (3) | 0.4665 (5) | 0.6338 (9) | 3.52 (11) |
| C(23) | 0.3680 (4) | 0.0612 (7) | 0.1967 (13) | 5.34 (18) |
| C(24) | 0.4303 (4) | 0.0787 (6) | 0.1773 (12) | 5.22 (15) |
| C(25) | 0.4683 (4) | 0.0032 (7) | 0.0970 (13) | 5.39 (16) |
| C(26) | 0.0570 (3) | 0.4075 (6) | 0.5379 (11) | 4.44 (13) |
| C(30) | 0.2069 (3) | 0.2230 (5) | 0.4858 (8) | 2.77[c] |
| C(31) | 0.2712 (2) | 0.2154 (4) | 0.5506 (8) | 2.94 (9) |
| C(32) | 0.2925 (3) | 0.1254 (5) | 0.6390 (9) | 3.62 (11) |
| C(33) | 0.3538 (3) | 0.1207 (6) | 0.7063 (11) | 4.70 (14) |
| C(34) | 0.3948 (4) | 0.2076 (6) | 0.6823 (12) | 4.85 (14) |
| C(35) | 0.3755 (4) | 0.2945 (6) | 0.5889 (12) | 4.91 (15) |
| C(36) | 0.3138 (3) | 0.3028 (5) | 0.5245 (10) | 3.99 (12) |
| C(1) | 0.2027 (7) | 0.1551 (13) | 0.0163 (20) | 4.47 (29) |
| C(2) | 0.1348 (7) | 0.1409 (11) | 0.0224 (18) | 3.77 (25) |
| C(3) | 0.1040 (7) | 0.2432 (14) | 0.0244 (19) | 4.26 (25) |
| C(4) | 0.1497 (9) | 0.3246 (11) | 0.0220 (19) | 4.11 (24) |
| C(5) | 0.2108 (8) | 0.2768 (16) | 0.0158 (22) | 4.97 (29) |
| C(1A) | 0.1222 (14) | 0.2819 (22) | 0.0181 (31) | 4.66 (42) |
| C(2A) | 0.1861 (12) | 0.3219 (16) | 0.0223 (27) | 4.10 (33) |
| C(3A) | 0.2221 (10) | 0.2272 (20) | 0.0164 (29) | 3.98 (39) |
| C(4A) | 0.1803 (13) | 0.1364 (18) | 0.0206 (33) | 4.62 (47) |
| C(5A) | 0.1198 (12) | 0.1816 (27) | 0.0202 (34) | 5.30 (49) |
| H(12)[d] | 0.039 (3) | 0.161 (5) | 0.661 (10) | *e* |
| H(13) | 0.481 (3) | 0.465 (5) | 0.734 (14) | |
| H(14) | 0.493 (3) | 0.344 (5) | 0.225 (13) | |
| H(15) | 0.378 (4) | 0.296 (6) | 0.092 (13) | |
| H(16) | 0.340 (3) | 0.475 (6) | 0.950 (12) | |
| H(22) | 0.195 (3) | 0.451 (5) | 0.657 (10) | |
| H(23) | 0.338 (3) | 0.071 (7) | 0.210 (15) | |
| H(24) | 0.468 (3) | 0.136 (6) | 0.213 (12) | |
| H(25) | 0.023 (3) | 0.493 (7) | 0.058 (13) | |
| H(26) | 0.033 (3) | 0.358 (6) | 0.449 (12) | |
| H(32) | 0.265 (3) | 0.083 (5) | 0.643 (10) | |
| H(33) | 0.367 (3) | 0.042 (6) | 0.731 (14) | |
| H(34) | 0.442 (3) | 0.192 (5) | 0.773 (12) | |
| H(35) | 0.408 (3) | 0.373 (6) | 0.549 (12) | |
| H(36) | 0.292 (3) | 0.369 (5) | 0.466 (11) | |

Anisotropic Temperature Factors[f] (×10$^4$)

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Ni | 19.4 (2) | 49.8 (6) | 121.8 (15) | −1.9 (3) | −0.6 (6) | −1.6 (13) |
| C(10) | 18.1 (13) | 45.6 (37) | 102 (10) | −4.9 (29) | 1.4 (29) | −3.0 (52) |
| C(20) | 20.1 (13) | 34.5 (35) | 122 (10) | 1.0 (18) | −5.9 (31) | 8.5 (51) |
| C(30) | 15.2 (13) | 50.2 (41) | 114 (10) | −2.9 (18) | 2.9 (29) | 1.8 (53) |

[a] Numbers in parentheses are esd's in the last figure quoted. [b] This value chosen arbitrarily to fix origin. [c] Equivalent isotropic *B*'s. [d] Hydrogen atoms have the same number as the carbon atoms to which they are bonded. [e] Hydrogen atom temperature factors were not refined but were fixed at one unit in *B* greater than the carbon atom to which they were bonded. [f] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

the final structure factor calculation[30] are given for the structure of polarity A (*vide supra*) in Table I. The rms amplitudes of thermal vibration and their direction cosines are given for the four atoms which were assumed to vibrate anisotropically in Table II.

## Results and Discussion

The crystal structure is built up of individual molecules of $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$. Views of the

TABLE II

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) AND THEIR DIRECTION COSINES[a] (IN PARENTHESES)

| Atom | Minor axis | Medium axis | Major axis |
|---|---|---|---|
| Ni | 0.185<br>(0.118, 0.242, 0.963) | 0.194<br>(0.370, 0.889, −0.269) | 0.211<br>(0.922, −0.388, −0.015 |
| C(10) | 0.169<br>(0.049, 0.254, 0.966) | 0.176<br>(0.568, 0.788, −0.236) | 0.212<br>(0.821, −0.560, 0.106) |
| C(20) | 0.157<br>(−0.155, 0.893, −0.422) | 0.187<br>(0.341, 0.449, 0.826) | 0.216<br>(0.927, −0.016, −0.374) |
| C(30) | 0.172<br>(−0.655, −0.333, 0.679) | 0.186<br>(0.574, 0.364, 0.733) | 0.202<br>(−0.491, 0.870, −0.047) |

[a] Direction cosines are referred to the orthorhombic crystal axes.

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[30] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

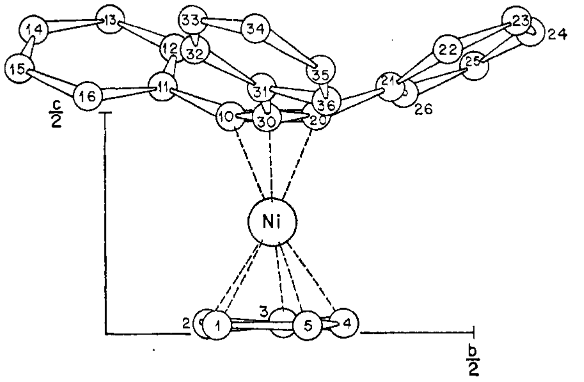

Figure 1.—A molecule of $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$ viewed along the crystallographic *a* axis. Only the principal orientation of the cyclopentadienyl group is shown.

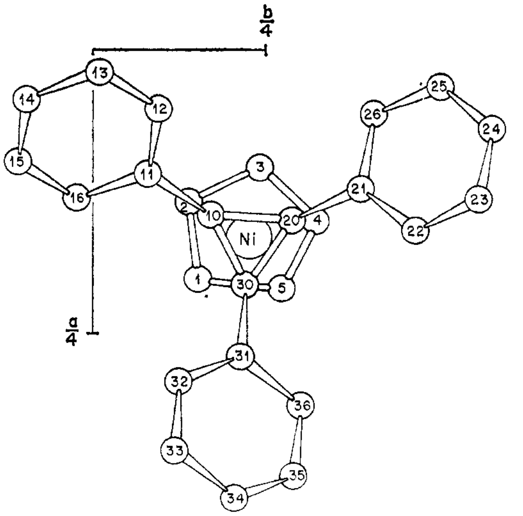

Figure 2.—A molecule of $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$ viewed along the crystallographic *c* axis. Only the princial orientation of the cyclopentadienyl group is shown.

molecule projected down the crystallographic *a* and *c* axes are shown in Figures 1 and 2, respectively. Selected interatomic distances and angles are given in Table III. The nickel atom is bonded in a *bona fide* "sandwich fashion" to the two essentially parallel (within 0.8°) aromatic five- and three-membered rings. Adopting the formalism that the tridentate π-cyclopentadienyl anion and the monodentate π-triphenylcyclopropenyl cation, respectively, donate six and two electrons, the four-coordinate $Ni^0$ atom achieves the rare gas configuration.

TABLE III

SELECTED INTERATOMIC DISTANCES AND ANGLES[a]

| | | | |
|---|---|---|---|
| **Bond Distances,[b] Å** | | | |
| Ni–C(10) | 1.953 (6) | Ni–C(30) | 1.968 (6) |
| Ni–C(20) | 1.961 (6) | Wtd av of 3 Ni–C | 1.961 (4) |
| Ni–C(1) | 2.13 (2) | Ni–C(1A) | 2.07 (2) |
| Ni–C(2) | 2.13 (1) | Ni–C(2A) | 2.10 (2) |
| Ni–C(3) | 2.14 (1) | Ni–C(3A) | 2.11 (2) |
| Ni–C(4) | 2.10 (1) | Ni–C(4A) | 2.09 (2) |
| Ni–C(5) | 2.08 (2) | Ni–C(5A) | 2.06 (3) |
| | | Wtd av of 10 Ni–C | 2.100 (6) |
| Ni–R(3)[c] | 1.779 | Ni–R(5)[c] | 1.726 |
| C(10)–C(20) | 1.427 (8) | C(10)–C(11) | 1.466 (8) |
| C(20)–3(30) | 1.437 (8) | C(20)–C(21) | 1.451 (8) |
| C(10)–C(30) | 1.421 (8) | C(30)–C(31) | 1.439 (8) |
| C(1)–C(2) | 1.44 (2) | C(1A)–C(2A) | 1.43 (4) |
| C(2)–C(3) | 1.42 (2) | C(2A)–C(3A) | 1.39 (3) |
| C(3)–C(4) | 1.39 (2) | C(3A)–C(4A) | 1.42 (3) |
| C(4)–C(5) | 1.41 (2) | C(4A)–C(5A) | 1.39 (4) |
| C(1)–C(5) | 1.51 (3) | C(1A)–C(5A) | 1.24 (4) |
| | | Wtd av of 10 C–C in Cp ring | 1.405 (9) |
| C(11)–C(12) | 1.381 (8) | C(12)–C(13) | 1.378 (9) |
| C(13)–C(14) | 1.381 (10) | C(14)–C(15) | 1.398 (11) |
| C(15)–C(16) | 1.377 (10) | C(11)–C(16) | 1.374 (8) |
| C(21)–C(22) | 1.369 (8) | C(22)–C(23) | 1.385 (11) |
| C(23)–C(24) | 1.334 (12) | C(24)–C(25) | 1.369 (12) |
| C(25)–C(26) | 1.371 (11) | C(21)–C(26) | 1.406 (8) |
| C(31)–C(32) | 1.370 (8) | C(32)–C(33) | 1.383 (10) |
| C(33)–C(34) | 1.388 (10) | C(34)–C(35) | 1.343 (11) |
| C(35)–C(36) | 1.389 (10) | C(31)–C(36) | 1.416 (8) |
| | | Wtd av of 18 C–C in phenyl groups | 1.378 (2) |
| **Angles,[b] Deg** | | | |
| C(30)–C(10)–C(20) | 60.6 (4) | C(10)–C(20)–C(30) | 59.5 (4) |
| C(20)–C(30)–C(10) | 59.9 (4) | C(30)–C(10)–C(11) | 144.6 (5) |
| C(11)–C(10)–C(20) | 143.7 (6) | C(10)–C(20)–C(21) | 146.4 (6) |
| C(21)–C(20)–C(30) | 144.5 (6) | C(20)–C(30)–C(31) | 143.9 (5) |
| C(31)–C(30)–C(10) | 144.6 (6) | R(3)–Ni–R(5) | 179.3 (2) |
| C(10)–C(11)–C(12) | 121.0 (5) | C(11)–C(12)–C(13) | 120.4 (6) |
| C(12)–C(13)–C(14) | 121.1 (7) | C(13)–C(14)–C(15) | 118.2 (7) |
| C(14)–C(15)–C(16) | 120.2 (7) | C(15)–C(16)–C(11) | 121.1 (7) |
| C(16)–C(11)–C(12) | 118.9 (6) | C(16)–C(11)–C(10) | 120.1 (6) |
| C(20)–C(21)–C(22) | 121.7 (5) | C(21)–C(22)–C(23) | 120.8 (7) |
| C(22)–C(23)–C(24) | 120.4 (8) | C(23)–C(24)–(25) | 120.7 (8) |
| C(24)–C(25)–C(26) | 120.2 (8) | C(25)–C(26)–C(21) | 119.9 (7) |
| C(26)–C(21)–C(22) | 118.0 (6) | C(26)–C(21)–C(20) | 120.3 (5) |
| C(30)–C(31)–C(32) | 121.6 (6) | C(31)–C(32)–C(33) | 121.0 (6) |
| C(32)–C(33)–C(34) | 119.8 (7) | C(33)–C(34)–C(35) | 119.9 (7) |
| C(34)–C(35)–C(36) | 121.5 (7) | C(35)–C(36)–C(31) | 119.0 (7) |
| C(36)–C(31)–C(32) | 118.7 (6) | C(36)–C(31)–C(30) | 119.8 (6) |
| C(1)–C(2)–C(3) | 110 (1) | C(2)–C(3)–C(4) | 109 (1) |
| C(3)–C(4)–C(5) | 109 (1) | C(4)–C(5)–C(1) | 108 (1) |
| C(5)–C(1)–C(2) | 103 (1) | C(1A)–C(2A)–C(3A) | 103 (2) |
| C(2A)–C(3A)–C(4A) | 109 (2) | C(3A)–C(4A)–C(5A) | 104 (2) |
| C(4A)–C(5A)–C(1A) | 111 (2) | C(5A)–C(1A)–C(2A) | 113 (2) |
| **Angles of Tilt of Phenyl Groups, Deg** | | | |
| [C(11), ···, C(16)][d,e] | 20.1 | [C(31)–C(36)] | 19.7 |
| [C(21), ···, C(26)][d,f] | 19.2 | | |
| **Angles of Twist of Phenyl Groups, Deg** | | | |
| [C(11), ···, C(16)] | 19.9 | [C(31)–C(36)] | 23.5 |
| [C(21), ···, C(26)] | 20.1 | | |

[a] These dimensions are for the structure of correct polarity (A). [b] Numbers in parentheses are the standard deviations in the last figure noted. [c] R(3) and R(5) are points at the centers of the cyclopropenyl and cyclopentadienyl rings, respectively. [d] [C(11), ···, C(16)] refers to the phenyl group containing carbon atoms C(11) through C(16). [e] This tilt angle is the supplement of the R(3)–C(10)–C(11) angle where R(3) is a point at the center of the cyclopropenyl ring. The other two tilt angles are similarly defined. [f] This twist angle is the complement of the dihedral angle between the [C(11), ···, C(16)] plane and the [Ni, R(3), C(10), C(11), C(14)] plane. The two remaining twist angles are similarly defined.

Within experimental error, the three Ni–C (cyclopropenyl ring) distances are equal to a mean value of 1.961 (4) Å which is very similar to the value[14] of 1.941 (5) Å determined in $(\pi\text{-}C_3(C_6H_5)_3)NiCl(py)_2$ (py = pyridine). The nickel–carbon distances for the π-cyclopentadienyl ring average 2.100 (6) Å which can be compared with a value of 2.107 Å found in an electron diffraction study[31] of $(\pi\text{-}C_5H_5)NiNO$. Perpendicular distances to the least-squares planes (see Table IV) through the three- and five-membered rings were found to be 1.779 and 1.726 Å, respectively, for the present complex. It appears that the perpendicular Ni–ring distance is the main factor controlling the distance of the nickel atom from the two rings. This is contrary to the results[13] discussed for $(\pi\text{-}C_5H_5)V$-

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(31) A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature (London)*, **181**, 1157 (1958).

TABLE IV

WEIGHTED[a] LEAST-SQUARES PLANES IN THE FORM $Ax + By + Cz + D = 0$[b]

| Plane no. | Atoms | $A$ | $B$ | $C$ | $D$ |
|---|---|---|---|---|---|
| 1 | C(1), C(2), C(3), C(4), C(5) | 0.0301 | −0.0019 | 0.9995 | −0.2474 |
| 2 | C(1A), C(2A), C(3A), C(4A), C(5A) | 0.0048 | −0.0041 | 1.0000 | −0.1512 |
| 3 | C(1), C(2), C(3), C(4), C(5), C(1A), C(2A), C(3A), C(4A), C(5A) | 0.0232 | −0.0026 | 0.9997 | −0.2208 |
| 4 | C(10), C(20), C(30) | 0.0129 | −0.0098 | 0.9999 | −3.6692 |
| 5 | C(11), C(12), C(13), C(14), C(15), C(16) | 0.4910 | 0.0840 | 0.8671 | −4.8022 |
| 6 | C(21), C(22), C(23), C(24), C(25), C(26) | −0.1589 | −0.4287 | 0.8894 | −1.2208 |
| 7 | C(31), C(32), C(33), C(34), C(35), C(36) | −0.3077 | 0.4065 | 0.8602 | −2.8712 |

Atoms and Their Distances from Planes, Å

| Plane no. | Atoms and distances |
|---|---|
| 1 | C(1), 0.000; C(2), 0.003; C(3), −0.004; C(4), 0.004; C(5), −0.002 |
| 2 | C(1A), −0.017; C(2A), 0.018; C(3A), −0.018; C(4A), 0.014; C(5A), 0.003 |
| 3 | C(1), −0.005; C(2), 0.008; C(3), 0.005; C(4), 0.006; C(5), −0.009; C(1A), −0.035; C(2A), 0.026; C(3A), 0.003; C(4A), 0.017; C(5A), −0.017 |
| 5 | C(11), 0.011; C(12), −0.010; C(13), 0.001; C(14), 0.011; C(15), −0.006; C(16), −0.007 |
| 6 | C(21), −0.007; C(22), 0.001; C(23), 0.009; C(24), −0.005; C(25), −0.013; C(26), 0.015 |
| 7 | C(31), 0.008; C(32), −0.012; C(33), 0.002; C(34), 0.020; C(35), −0.022; C(36), 0.004 |

Dihedral Angles

| Planes | Angle, deg | Planes | Angle, deg |
|---|---|---|---|
| 3,4 | 0.7 | 4,6 | 27.0 |
| 4,5 | 29.3 | 4,7 | 31.6 |

[a] Atoms are weighted by the reciprocals of their variances. [b] The orthogonal coordinates correspond to the crystal axes *a*, *b*, and *c*, respectively, and are in ångström units.

TABLE V

DISTANCES (Å) IN SOME NICKEL COMPLEXES OF CARBOCYCLIC RINGS[a]

| Complex | No. of carbon atoms in ring | Ni–C-(ring), Å | Range, Å | Ni–ring, Å |
|---|---|---|---|---|
| $(\pi\text{-}C_3(C_6H_5)_3)NiCl(py)_2$[b] | 3 | 1.941 (5) | 1.896–1.968 | 1.759 |
| $(\pi\text{-}C_3(C_6H_5)_3)Ni(\pi\text{-}C_5H_5)$[c] | 3 | 1.961 (4) | 1.953–1.968 | 1.779 |
| $[(\pi\text{-}C_4(CH_3)_4)NiCl_2]_2$[d] | 4 | 2.022 (6) | 1.997–2.047 | 1.749 |
| $[(\pi\text{-}C_5H_5)Ni(P(C_6H_5)_2)]_2$[e] | 5 | 2.10 (1) | 2.06–2.14 | 1.74 |
| $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$[c] | 5 | 2.100 (6) | 2.060–2.137 | 1.726 |
| $(\pi\text{-}C_5H_5)NiNO$[f] | 5 | 2.107 (1) | | 1.72 |
| $(\pi\text{-}C_5H_5)Ni(P(C_6H_5)_3)CF_3$[g] | 5 | 2.11 (1) | 2.06–2.16 | 1.76 |
| $(\pi\text{-}C_5H_5)_2Ni_2C_2(C_6H_5)_2$[h] | 5 | 2.11 (1) | 2.05–2.16 | 1.74 |
| $(\pi\text{-}C_5H_5)NiC_4(CH_3)_4C_5H_5$[i] | 5 | 2.132 (8) | 2.098–2.168 | 1.764 |
| $(\pi\text{-}C_5H_5)NiC_5H_5C_2(COOCH_3)_2$[j] | 5 | 2.130 (6) | 2.096–2.148 | 1.75 |
| $(\pi\text{-}C_5H_5)Ni(P(C_6H_5)_3)C_6H_5$[k] | 5 | 2.139 (4) | 2.087–2.195 | 1.776 |
| $(\pi\text{-}C_5H_5)Ni(P(C_6H_5)_3)C_6F_5$[l] | 5 | 2.144 (8) | 2.107–2.184 | 1.769 |
| $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$[m] | 5 | 2.15 | 2.13–2.17 | 1.78 |
| $(\pi\text{-}C_5H_5)Ni$[n] | 5 | 2.196 (4) | | 1.83 |

[a] Standard deviations are given in parentheses. [b] Reference 14. [c] This work. [d] J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962). [e] J. M. Coleman and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 542 (1967). [f] Reference 31; microwave value. [g] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 161 (1970). [h] O. S. Mills and B. W. Shaw, *J. Organometal. Chem.*, **11**, 595 (1968). [i] W. Oberhansli and L. F. Dahl, *Inorg. Chem.*, **4**, 150 (1965). [j] L. F. Dahl and C. H. Wei, *ibid.*, **2**, 713 (1963). [k] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 266 (1969). [l] M. R. Churchill and T. A. O'Brien *ibid.*, *A*, 2970 (1969). [m] A. A. Hock and O. S. Mills, "Advances in the Chemistry of Coordination Compounds," Macmillan, New York, N. Y., 1961. [n] L. Hedberg and K. Hedberg, *J. Chem. Phys.*, **53**, 1228 (1970); electron diffraction value.

($\pi$-$C_7H_7$) where the vanadium–carbon atom distances were found to be constant for the two different rings: V–$C_7H_7$ = 2.25 Å and V–$C_5H_5$ = 2.23 Å. However, for nickel complexes of $\pi$-ring systems ($C_3R_3$ to $C_5H_5$) the nickel–ring distance is approximately constant and the Ni–C(ring) distances increase to maintain this constancy as the number of carbon atoms in the carbocycle increases—see Table V. Because of the current paucity of X-ray diffraction data for "mixed sandwich" compounds—($\pi$-$C_5H_5$)Ni($\pi$-$C_3(C_6H_5)_3$) and ($\pi$-$C_5H_7$)V($\pi$-$C_7H_7$) appear to be the only two complexes of this type studied to date—it is uncertain whether the metal–C(ring) or metal–ring contacts are the major factor in determining the approach of a metal atom to a $\pi$-ring system. Moreover, for complexes with a metal atom $\pi$ bonded to only one ring, it is difficult to assess the electronic and/or steric demands of the atoms or groups of atoms bonded to the metal atom on the other side.

Carbon–carbon distances in the cyclopropenyl ring are equal, within 2$\sigma$, to an average value of 1.428 (5) Å which may be compared with the distance of 1.421 (8) Å found in ($\pi$-$C_3(C_6H_5)_3$)NiCl(py)$_2$. Both of these lengths are longer than that determined[32] for the free ligand (1.373 (5) Å) in ($C_3(C_6H_5)_3$)($ClO_4$). An increase of this magnitude for the C–C distances in a ring is typical of metal $\pi$ complexes of this type.[33] The average exocyclic C–C bond lengths of 1.452 (4) and 1.436 (3) Å for ($\pi$-$C_5H_5$)Ni($\pi$-$C_3(C_6H_5)_3$) and ($C_3(C_6H_5)_3$)($ClO_4$), respectively, are shortened relative to the value of 1.48 Å accepted for a C(sp$^2$)–C(sp$^2$) single-bond distance. This trend may be attributed to conjugation between the phenyl substituents and the positively charged cyclopropenium ring and probably more importantly to a greater s character than that of a pure sp$^2$ hybrid for the carbon orbitals directed toward the phenyl groups.

Eight of the ten distances found in the disordered Cp ring are well within the expected range. The average value of 1.405 (9) Å (for all 10 carbon atoms) is 0.01 Å shorter than the average noted[33] for 23 structures containing this ring. Average distances and angles in the phenyl groups are those expected. The average of 15 C–H distances is 1.02 Å.

The three phenyl groups are both tilted out of the plane of the cyclopropenyl ring away from the nickel atom and twisted about their respective axes (in the same sense) by about 20° to produce a "propeller" configuration. Deviations from planarity of substituent groups have been noted in other metal $\pi$-ring complexes such as ($\pi$-$C_4(C_6H_5)_4$)Fe(CO)$_3$.[34] In certain cases a finite tilt angle has been ascribed by Kettle[35] to a mixing of $\sigma$ and $\pi$ orbitals on the ring in an effort to attain maximum overlap between the ring and metal atom orbitals. In Kettle's treatment the two assumptions are made that the principal bonding interactions between the metal atom and the ring are of an e type and that there are no conjugation effects between the ring substituents and the $C_n$ ring. Neither of these assumptions is thought to be valid for ($\pi$-$C_5H_5$)Ni($\pi$-$C_3(C_6H_5)_3$) and hence a quantitative application of this theory is not possible in the present case. The rotation of the phenyl groups is probably the result of intramolecular van der Waals forces with the three

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[32] M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

[33] P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 1 (1967).

[34] R. P. Dodge and V. Schomaker, *Acta Crystallogr.*, **18**, 614 (1965).

[35] S. F. A. Kettle, *Inorg. Chim. Acta*, **1**, 303 (1967).

contacts C(16)–H(32), C(26)–H(12), and C(36)–H(22) being implicated. In $(C_3(C_6H_5)_3)(ClO_4)$ it was found[32] that a strain-free condition of the phenyl groups was produced for an average twist angle of 14° and 0° tilt angle. Since the phenyl groups are pushed out of the ring toward each other by about 20° in the present complex, a larger twist angle results in order to relieve the repulsion between these groups.

The crystal structure viewed along axes *a* and *c* is shown in Figures 3 and 4, respectively. All of the distances (range 3.4–3.7 Å) closer than those expected from van der Waals radii are between carbon atoms of the phenyl groups in one molecule and the cyclopentadienyl ring of the molecule removed by one unit translation in the *c* direction. Thus the crystal packing appears to be controlled by the stacking of molecular units in this direction.

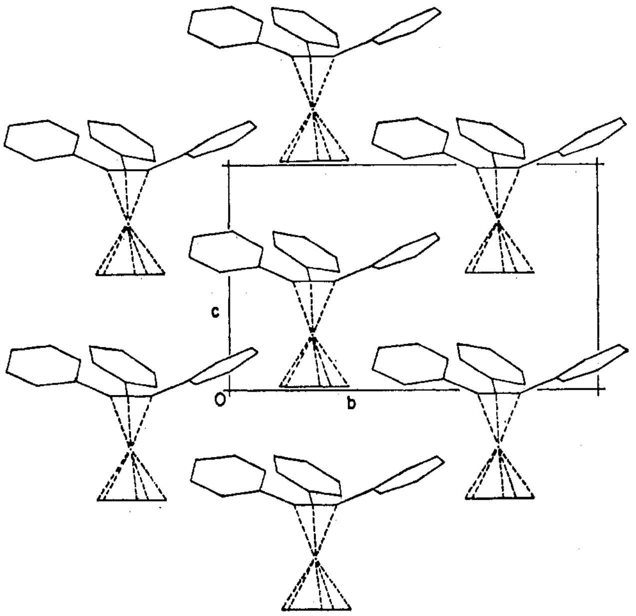

Figure 3.—Molecular packing of $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$ projected down the crystallographic *a* axis.

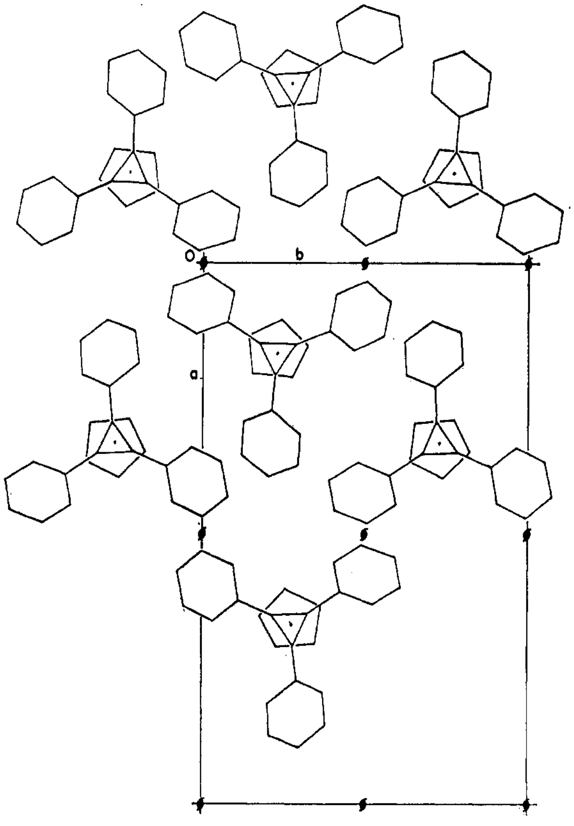

Figure 4.—Molecular packing of $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$ projected down the crystallographic *c* axis.

A simplified discussion of the bonding in the present complex is possible if the molecule is subdivided into two parts—$(\pi\text{-}C_5H_5)Ni$ and $Ni(\pi\text{-}C_3(C_6H_5)_3)$—with localized $C_{5v}$ and $C_{3v}$ symmetry, respectively. For the $(\pi\text{-}C_5H_5)Ni$ part, the following interactions are possible: (1) overlap of a metal $a_1$ orbital ($3d_{z^2}$, 4s, and $4p_z$ contributions) and the $a_1$ combination of the cyclopentadiene $p\pi$ orbitals and (2) overlap of the $e_1$ metal orbitals ($d_{xz}$, $d_{yz}$) and the $e_1$ combination of the $C_5$ ring $p\pi$ orbitals. In addition, the empty $e_2$ antibonding combination of ring $p\pi$ orbitals could provide a pathway for back-donation from the metal $e_2$ orbitals ($d_{x^2-y^2}$, $d_{xy}$). Two interactions are feasible for the $Ni(\pi\text{-}C_3(C_6H_5)_3)$ portion of the molecule: (1) overlap of an $a_1$ metal orbital ($3d_{z^2}$, 4s, and $4p_z$ contributions) with the $a_1$ combination of the $C_3$ $p\pi$ orbitals and (2) back-donation from the metal e orbitals ($d_{xz}$, $d_{yz}$) to the e antibonding combination of the $C_3$ ring $p\pi$ orbitals. Presumably, if back-donation occurred, more would be possible to the $C_3$ than the $C_5$ ring since the former has *formally* associated with it a positive charge.

The preceding bonding description is not unlike that given for $(\pi\text{-}C_5H_5)NiNO$.[36] It is interesting in this regard to consider the isoelectronic series of nitrosyl derivatives—$(\pi\text{-}C_5H_5)CrNO(CO)_2$,[37] $(\pi\text{-}C_5H_5)MnNO(CO)_2^+$,[38] $\{(\pi\text{-}C_5H_5)FeNOCO\}$, $\{(\pi\text{-}C_5H_5)CoNOCO^+\}$, and $(\pi\text{-}C_5H_5)NiNO$,[31,36] where the compounds in braces have not as yet been prepared. It is possible that an analogous series of cyclopropenyl complexes may exist, namely, $(\pi\text{-}C_5H_5)Cr(\pi\text{-}C_3(C_6H_5)_3)(CO)_2$, $(\pi\text{-}C_5H_5)Mn(\pi\text{-}C_3(C_6H_5)_3)(CO)_2^+$, $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_3(C_6H_5)_3)CO$, $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_3(C_6H_5)_3)CO^+$, and $(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_3(C_6H_5)_3)$. The molybdenum analog[12] of the first member of this series and the nickel complex discussed herein are currently known.

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